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Influence of vacuum mixing on the carbonation resistance and microstructure of reactive powder concrete containing secondary copper slag as supplementary cementitious material (SCM)

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Abstract

This study aims to examine the effect of vacuum mixing on the carbonation resistance and microstructure of reactive powder concrete (RPC), made with secondary copper slag as partial cement replacement. In order to obtain a homogenous mixture, a high speed mixer with vacuum was applied. Accelerated carbonation tests (10% CO_2, 20°C and 60% RH) were performed on RPC, mixed under vacuum conditions, as a comparison to RPC mixed at atmospheric pressure. The evolution of the carbonation depth was determined by spraying phenolphthalein on a freshly split RPC surface at varying ages (1 to 16 weeks). The microstructure of RPC was investigated by a mercury intrusion porosimeter (MIP). The pozzolanic activity of QCS was determined by the Chapelle test, taking into account the carbonation effect on the reference system.

The results obtained, showed that no carbonation was detected after 90 days for the RPC containing copper slag both under vacuum condition and atmospheric pressure. The presence of copper slag in the RPC tends to increase the porosity reduction and decrease the strength enhancement when applying vacuum mixing to the mixture. The result of the Chapelle test indicated that the secondary copper slag did not tend to consume much portlandite.

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Keywords : Secondary copper slag; vacuum mixing; carbonation; microstructure; pozzolanic activity.

1. Introduction

Reactive powder concrete (RPC) is a new breakthrough of concrete technology. The production of this concrete needs a huge amount of cement to improve the concrete strength, which implies high cost. Concrete with higher

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cement content can cause high heat generation from cement hydration and this phenomenon can lead to the formation of micro cracks, which will allow liquids and gases (e.g. CO_2) to penetrate into concrete. In the end, ingress of CO_2 will accelerate carbonation in concrete and it will cause the deterioration of reinforced concrete [1]. As a consequence, the service life of the concrete structures will decrease. Although, due to the high cement content, not all of the cement is perfectly hydrated, the large amount of portlandite in the concrete matrix has potency to react with CO_2 to generate $CaCO_3$. The process of portlandite carbonation is fast, in which more than 80% carbonation of $Ca(OH)_2$ is achieved in 2 hours contact with liquid CO_2 in ambient temperature [2]. In order to overcome this problem, the use of secondary copper slag as cement replacement and vacuum mixing are investigated in this paper, as a means to minimize potential concrete carbonation.

One measure to obtain a void-free mixture is to use an intensive vacuum mixing in which this mixer can remove air content. A void-free mixture contributes to the strength and service life of concrete. This is confirmed by the results of Dils, et al. [3]. They concluded that the compressive strength increases when the air content decreases in the UHPC mixture.

Typical by-products that are already widely used in concrete are e.g. fly-ash and blast-furnace slag. Copper slag is one of the by-product materials from the copper smelting. Every year, about 24.6 million tons of copper slag are produced by the copper industry throughout the world [4]. In Europe, approximately 5.56 million tons of copper slag are generated by the European copper industry [4], and in Belgium, about 132,240 tons of secondary copper slag are produced in recycling plants annually [5,6]. Since this material needs a large area for landfilling, of which the availability is insufficient, and to avoid problems related to the leaching of heavy metals and other harmful elements, it would be interesting to upgrade these 'waste' products in high-value applications. Moreover, the amount of natural resources is declining due to a large consumption in the cement and concrete production. A possible breakthrough can thus be sought in exploiting these by-products within cement and concrete production. This paper presents the influence of vacuum mixing on carbonation and microstructure of RPC containing copper slag as cement replacement. The Chapelle test was chosen to assess the pozzolanic activity of secondary copper slag.

2. Material and experimental procedure

2.1. Material

The materials used in this study were purchased from Belgian and German companies except for the secondary copper slag, which was obtained from a Belgian Recycling Plant. The secondary slag used in this research was quickly cooled granulated copper slag (QCS). This slag was produced by using primary slag from Cu such as old copper tubes, wires, scraps, cables, alloy coins, plated coins and Cu-Fe (shredded) armatures as raw materials to generate copper blister, copper anodes, and copper cathodes for industry and market. Another binder used in this research was dry undensified silica fume (940U, Elkem), which has a typical bulk density of 200-350 kg/m3. As cement, a CEM I 52.5 N HSR/LA was used throughout all experiments. For all concretes, a quartz flour (type M400, Sibelco) with a d50 of 12 μm was used. An overview of the chemical composition of the powders is given in Table 1.

Since the copper slag obtained by the recycling plant was in granulate form, the size of this slag has to be reduced to achieve a product with a higher specific surface area (SSA). The selection of the appropriate method of grinding should be based on the physical properties of the materials. Copper slag has a toughness of 6-7 Mohs hardness and is mainly composed of iron silicate glass [4,7]. Therefore, there will be a high energy need to grind this material. In the grinding process, the energy is determined by the time, speed, and number of balls charged. Based on the results obtained by Edwin, at al. [8], the SSA of QCS was 2533 cm^2/g with the Blaine permeability test. This result can be achieved using the dry method, long duration of grinding (5 times during 12 minutes at 300 rpm) and 5 balls charged. This grinding process was time-consuming and not very productive. In order to reduce the time for the grinding process, the authors now chose a short duration (6 times during 5 minutes at 390 rpm) and 7 balls charged. This method reduced the grinding time with 30 minutes in comparison with that of the long duration method. With the increase in grinding speed and addition of two balls in this method it was expected to achieve a similar fineness as with the grinding method aforementioned. Besides, copper slag tends to be re-compacted when applying a dry method. These are the reasons to choose a wet method instead of dry method. A superplasticizer (Sika Viscocrete-3095x; 0.122

wt%) was chosen to avoid re-compaction. After the grinding process, the particle size distribution (PSD) of copper slag powder was measured by laser diffraction with the size range from 0.1 μm to 1000 μm.

Table 1. Chemical Composition of the Applied Powders Determined by XRF Analysis [wt.%]

Material	QCS	Cement	Silica fume	Flour (M400)
CaO	7.1	63.4	0.6	0.02
SiO_2	25.9	21.5	94.2	99.5
Al_2O_3	5.9	3.6	1.0	0.2
Fe_2O_3	45.5	4.2	0.5	0.03
MgO	0.8	1.6	0.7	n/a
Na_2O	0.8	0.2	1.0	n/a
K_2O	0.2	0.6	1.1	0.05
SO_3	0.4	2.5	0.3	n/a
P_2O_5	0.8	n/a	0.1	n/a
TiO_2	0.3	n/a	n/a	n/a
ZnO	8.8	n/a	n/a	n/a
MnO	0.7	n/a	n/a	n/a
Cr_2O_3	0.7	n/a	n/a	n/a
CuO	0.4	n/a	n/a	n/a
Pb	0.4	n/a	n/a	n/a

The particle size distribution of copper slag, silica fume, and quartz flour obtained by laser diffraction is given in Figure 1. To disperse this material, isopropanol was used since it does not react with copper slag. To avoid agglomeration, the copper slag was put in a sonication bath (5 min) before the measurement. In case of silica fume, distilled water was used as dispersant. In order to obtain well de-agglomerated silica fume, this material was sonicated in two steps. At first, the solution containing silica fume and water was put in an ultrasonic bath for 5 minutes to de-agglomerate the particles. After this, 10% superplasticizer by weight of silica fume was added followed by sonication for 15 minutes prior to measurement. An overview of the parameters used to determine the PSD of the SCMs, cement, and quartz by laser diffraction can be seen in Table 2.

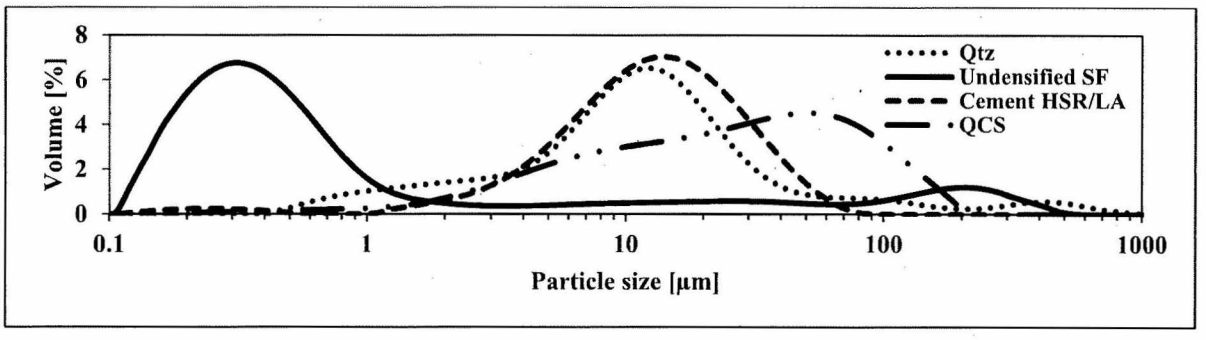

Fig. 1. Particle Size Distribution by Laser Diffraction of the Different Powders

In addition to the PSD by laser diffraction, the fineness of the binders was evaluated by their specific surface area (SSA) using the Blaine air permeability test according to NBN EN 196-6:2010. To start, the pycnometer method was used to measure the density of all powders. Both the density and SSA of the powders are presented in Table 3.

Table 2. Overview of the Parameters Applied to Determine the PSD of the Different Powders by Laser Diffraction

Optical parameters	QCS	Silica fume	CEM I	Quartz flour (Qtz)
Refractive index (RI) [-]	1.731	1.530	1.731	1.55
Absorption coefficient [-]	0.055	0.001	0.003	0.3
Obscuration [%]	10 - 15	5 - 10	5 – 10	5 – 10
Stirrer rate [rpm]	1700	1500	1500	1700
Dispersant RI [-]	1.390	1.390	1.390	1.390
Sonication times [minutes]	5	20	5	5

Table 3. Density and SSA of the Different Powders

Materials	QCS	CEM I	Silica fume	Quartz flour (Qtz)
Density (g/cm^3)	3.706	3.152	2.017	2.65
SSA (cm^2/g) :				
Blaine permeability	2277	4955	-	6500
Laser diffraction	2150	5390	56200	5444

2.2. Mixing procedure

In this research, the authors used a planetary vacuum mixer with a capacity of 5 liter. The procedure of mixing follows the method shown in [9]. First the dry materials were poured in the inclined drum. They were mixed during 15 s at 255 rpm. Afterwards, the water and superplasticizer were dosed. After the non-vacuum phase, the maximum speed mixing (910 rpm) was started for 150 s and at the same moment the vacuum phase was applied for 270 s. In the last 120 s of the vacuum phase, the speed was reduced to 255 rpm. In the case of non-vacuum mixing, the same method was applied after dosing the water and superplasticizer, with the mixer set at atmospheric pressure (1013 mbar).

2.3. Carbonation depth and mercury intrusion porosimetry (MIP)

After mixing, the fresh concrete was cast in molds with dimensions of 40 mm x 40 mm x 160 mm. Subsequently, they were stored for 2 days at 20°C and RH > 95%. Afterwards, the specimens were removed from the molds and cured at 20°C and RH > 95% for 90 days. Before the start of the accelerated carbonation test, a freshly split surface of the samples was sprayed with phenolphthalein to obtain the initial value of the carbonation depth. Five surfaces of the samples were coated with epoxy, leaving one surface exposed in a climate chamber (20 ± 2°C, RH 60 ± 5%) to 10% CO_2. The carbonation ingress was measured with phenolphthalein after 4, 8 and 16 weeks.

To investigate the influence of vacuum mixing on the porosity, mercury intrusion porosimetry (MIP) was performed on the RPC samples. In order to preserve the pore structure of the specimens, the freeze-drying method was chosen. The specimens for MIP are defined as crushed particles with particle size between 5 and 10 mm. After putting these specimens in the liquid nitrogen for 5 minutes, the temperature of the sample was reduced to -195°C. Afterwards, the samples were transferred into a freeze-dryer and the temperature changed to -24°C under vacuum condition and pressure of 0.1 Pa [10]. After four weeks, a constant mass was obtained (mass change less than 0.1% in 24 hours). After the period of freeze-drying, a sample of ± 1.40 g was put into a dilatometer (Thermo Scientific Corporation) to start the measurement. The mercury was intruded into the specimen and extruded after reaching the maximum pressure. This porosity measurement of the sample was determined using 140 Pascal for the low pressure and 440 Pascal for the high pressure.

3. Results and discussions

3.1. Carbonation depth

The carbonation depth for both the samples mixed under vacuum condition (100 mbar) and atmospheric pressure (1013 mbar) which was measured on a freshly split RPC surface using 1% phenolphthalein in 70% ethyl alcohol shows no carbonation up to 16 weeks, as seen in Table 4. Both the reference RPC and the mixtures with copper slag show zero carbonation, as also shown in Table 4. These results confirm that the concrete with low porosity and very dense microstructure has an excellent carbonation resistance [11]. The CSH gel will fill the concrete pores and limit the CO2 penetration into the concrete. However, the effect of the vacuum mixing and copper slag replacement on the carbonation of RPC is unclear since there is no carbonation detected even in non-vacuum mixing and reference mixture. Therefore, long-term exposure in a climate chamber (e.g. 32 or 64 weeks) is required for RPC to determine the effect of vacuum mixing and copper slag replacement on the carbonation resistance.

Table 4. Results of carbonation test on RPC containing copper slag

Exposure time	Reference		5% CS		10% CS		15% CS		20% CS	
	Vac	N-Vac	Vac	N-Vac	Vac	N-Vac	Vac	N-Vac	Vac	N-Vac
4 weeks	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
8 weeks	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
16 weeks	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note. ND = not detected

3.2. Mercury intrusion porosimetry and compressive strength

Figure 2 describes the effect of vacuum mixing on the porosity of RPC containing copper slag as cementitious material. In general, the porosity of RPC mixed under vacuum (100 mbar) and at atmospheric pressure (1013 mbar) decreased with rising copper slag content in RPC mixture at 56 days in comparison with the reference mixture without copper slag. The lowest porosity (4.91%) was achieved for 15% copper slag replacement under vacuum mixing, which decreased about 18.4% compared to the reference specimens. This achievement also occurred for 15% copper slag substitution under non-vacuum condition, which induced a decrease of about 11.4% in porosity compared to control mixtures.

The influence of vacuum mixing on the compressive strength of RPC containing copper slag as cement replacement is shown in Figure 3. It seen that the strength of RPC under vacuum condition increases with rising copper slag substitution in the concrete mixture. The highest compressive strength (158 MPa) is achieved for 10% copper slag. However, this achievement is contradictory with the result of RPC non vacuum, which is similar or (slightly) lower for the RPC with copper slag than for the reference mixture.

Based on the result obtained in Figure 2 and Figure 3, it is necessary to study the influence of vacuum mixing on the porosity reduction and the strength enhancement of RPC containing copper slag.

The influence of vacuum mixing on the reduction of porosity is the highest for the mixtures with 20% copper slag replacement. A decrease of about 22% is seen (Figure 4). Nonetheless, the RPC mixtures with 5% and 10% copper slag replacement showed low porosity reduction, which was less than for the reference mixture. From this result, it can be stated that the effect of vacuum mixing on the porosity of RPC mixtures containing small amounts of copper slag is limited. For higher amount of copper slag replacement, the vacuum mixing contributed more to reduce the porosity of RPC. This achievement is mainly caused by the physical properties of copper slag. Looking into the literature, the angular sharp edges of the copper slag can improve the cohesion of the concrete matrix [12, 13, 14, 15]. This property has the ability to fill out the air cavities which are removed by vacuum mixing. Nevertheless, due to the differences in homogeneity and complexity of the pore structure, the pore cavities of RPC cannot be successfully filled by copper slag, leaving certain amount of unfilled porosity.

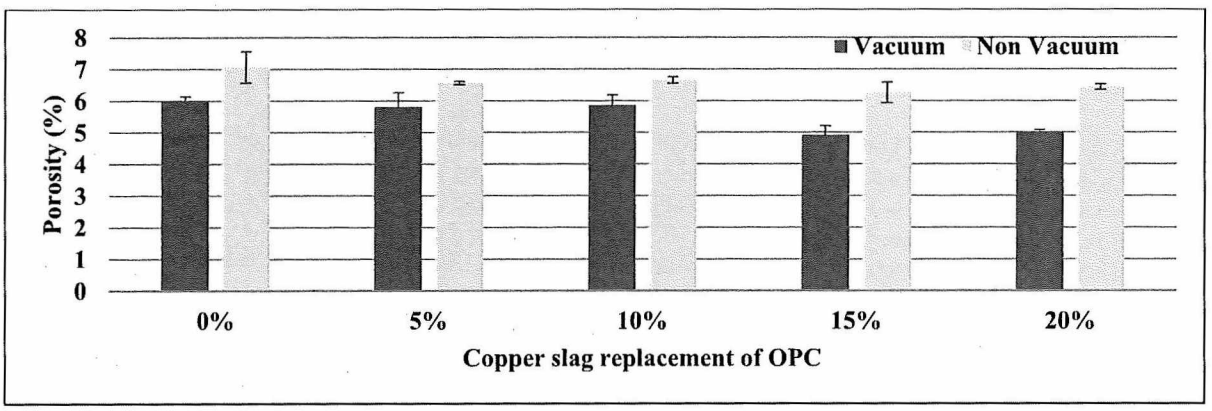

Fig. 2. Influence of mixing procedure (vacuum condition (100 mbar) and atmospheric pressure (1013 mbar)) and copper slag replacement on the porosity of RPC at 56 days (error bars represent standard errors, the average values represent two replicates)

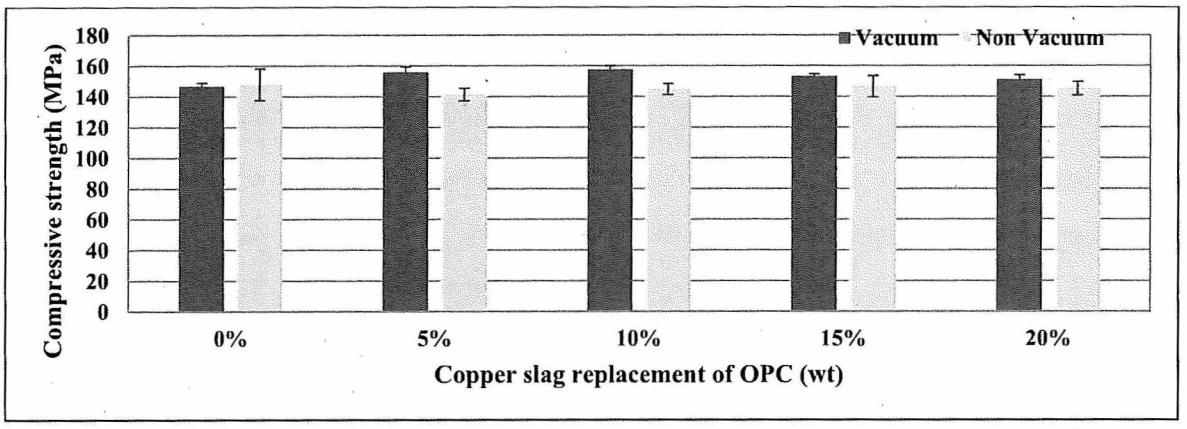

Fig. 3. Strength of RPC mixed under Vacuum (100 mbar) and Atmospheric Pressure (1013) at 56 days (error bars represent standard errors, the average values represent three replicates)

The RPC with 0% copper slag showed a compressive strength of 148 MPa when mixed under atmospheric conditions and 147 MPa under vacuum. The strength enhancement for mixes with larger replacement levels (15% and 20%) due to vacuum condition was lower than for mixes with a small quantity of copper slag replacement (5% and 10%), as shown in Figure 4. This result is contradictory with the porosity reduction under vacuum mixing, which was the highest for 15% and 20% copper slag replacement. This finding is in contrast with the result obtained by several researchers [16, 17]. In their research, they proposed a model relationship between compressive strength and total void ratio. They concluded that the compressive strength of high performance porous concrete (HPPC) was increased with decreasing total void ratio. This current finding can easily be explained by the fact that the increase in compressive strength of concrete is not only caused by porosity reduction, but it is also determined by CSH gel generated during the hydration process. The latter corresponds well to the strong bond in concrete matrix. Moreover, vacuum mixing only contributes to reduce the porosity of RPC. Copper slag reacts with the portlandite to produce CSH gel. Due to the insufficient fineness of this slag, only a small amount of copper slag reacts to generate CSH gel. This can also be explained by the fact that only around 35% of calcium oxide (CaO) is consumed by copper slag in the Chapelle test, as seen below in Figure 5. For larger replacement levels (e.g. 15% and 20%), the amount of CSH gel does not increase, leaving certain amount of unreacted copper slag in concrete matrix. The copper slag shows angular sharp edges, and it will contribute as filler in the concrete matrix. This is the reason for decreasing the porosity of RPC containing higher amount of copper slag.

From Figure 4, it can be stated that the porosity reduction under low air pressure for higher amount of copper slag replacement is double than that of the RPC containing small amount of copper slag. In contrast to the porosity reduction, the strength enhancement for larger replacement levels (15% and 20%) under vacuum mixing is halved compared to low replacement levels.

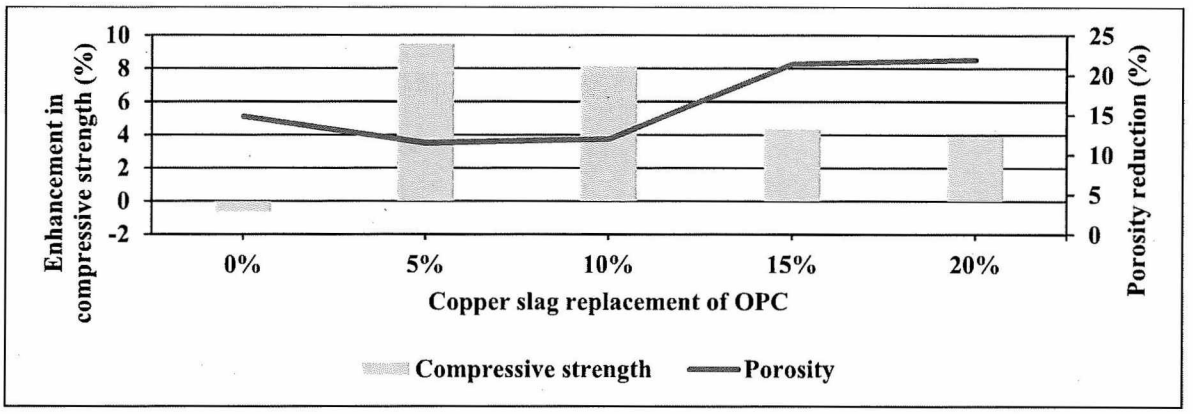

Fig. 4. Relative influence of vacuum mixing versus mixing at atmospheric pressure on the porosity and strength enhancement of RPC at 56 days

3.3. Chapelle test

The results of the Chapelle test are shown in Figure 5. In this study, the result of the reference indicated that a significant amount of portlandite had reacted although the system was built to avoid carbonation. Based on the amount of portlandite carbonated in the reference system, a formula is used to correct the results of the mixes with copper slag and quartz powder [18] :

$$CH_{corr} = \frac{CH_{calc} - CH_{ref}}{CH_i - CH_{ref}} \quad (1)$$

where

CHcorr is the corrected consumed calcium hydroxide.
CHcalc is the calculated consumed calcium hydroxide.
CHref is the consumed calcium hydroxide for the reference.
CHi is the initial calcium hydroxide.

Looking into the literature, the amount of portlandite consumed by copper slag in this research was lower than for the three pozzolanic materials (metakaolin, fly ash and natural pozzolans) used in [18]. This is mainly due to the different chemical composition of the SCMs used by the author and [18]. The chemical reaction rate to form C-S-H gel is determined by the calcium and siliceous content in SCMs. The calcium-poor and siliceous-rich fractions of pozzolans (metakaolin, fly ash, and natural pozzolans) rapidly consume large amounts of portlandite. Conversely, the calcium-poor and siliceous-moderate secondary copper slag used in the current research tends to consume less portlandite.

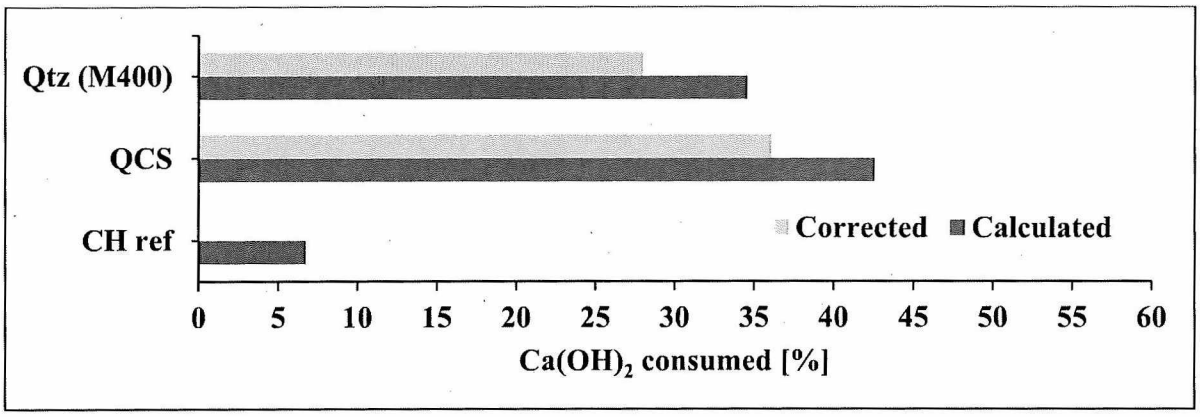

Fig. 5. Amount of Ca(OH)2 consumed by 1g of difference types of powder

4. Conclusions

Concerning the effect of vacuum mixing on carbonation and microstructure of RPC containing secondary copper slag as cementitious material, the following conclusions can be drawn:

1. A zero level of carbonation is found for RPC containing copper slag and mixed under vacuum and at atmospheric pressure. This is mainly caused by the low porosity and the very dense microstructure of RPC which increase the resistance against carbonation.
2. By applying vacuum mixing to the RPC mixture, the porosity decreased. The reduction is higher with increasing copper slag content. This result is in contrast with the compressive strength enhancement of RPC, which decreased for larger replacement levels of copper slag.

Assessment of the pozzolanic activity using the Chapelle test indicates low pozzolanic activity of secondary copper slag used in this research. This phenomenon indicates that the amount of CSH gel produced during hydration is limited. However, the porosity reduction of RPC is enhanced by the physical properties of copper slag.

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